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Potential and limitation of straight vegetable oils as engine fuel – An Indian perspective

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ABSTRACT

Due to rapid price increase in petroleum fuels, there is a growing demand for the search for sustainable, environment friendly and cost effective alternative substitute renewable fuel. Out of various available sources straight vegetable oils (SVOs) from edible oil and non-edible oil resources abundantly available in India are selected. Five edible and four non-edible selected SVOSs are analysed on the basis of composition of fatty acids. Oxidation Stability Index and cold flow properties are computed and SVOs are graded for biodiesel production. The result found that SVOs in order of decreasing OSI are Castor > Mahua > Neem > Karanja can be recommended as potential feed stocks for biodiesel production while other SVOs are not due to their instability but may require considerable effort to make the fuel stable. CP and CFPP of edible SVOs in decreasing order are found: Castor > Rape seed > canola > Soya bean while non-edible SVOs in decreasing order are Mahua > Neem > Karanja > Jatropha > Soybean indicating that there is a need to improve the cold flow properties using additives. Out of all SVOs the Castor oil has highest OSI and good cold flow properties and recommended as the best SVO for biodiesel production.

Contents

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1. Introduction

The world is confronted with the crises of fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of fossil fuels coupled with serious environment degradation has led to the fast depletion of finite and highly concentrated fossil resources all over the world [1]. India imports more than 80% of petroleum crude and is putting heavy burden on exchequers. The situation can be improved by developing alternative biofuels like biodiesel and bioethanol as substitute of petroleum diesel and gasoline respectively. The biodiesel can be produced from renewable feedstock such as edible and non-edible oils [1,2]. The edible oils are used to meet the demand of food and more than 50% of total edible oil consumption is still imported in India and therefore there is no possibility of diverting edible oils for biodiesel production. The attention is then diverted to non-edible resources. Lots of research is available worldwide on the use of straight vegetable oils (SVOs) as engine fuel as substitute of petroleum diesel [3]. SVOs being renewable, are widely available from a variety of sources, with low sulphur contents close to zero, and hence cause less environmental damage than diesel. Altin et al. [4] found SVOs to have high energy contents and most require some processing to assure safe use in internal combustion engines. Some of these oils have already been evaluated as substitutes for diesel fuels. Ramadhas et al. [5] reported that SVOs can be directly mixed with diesel to operate the engines. Agarwal et al. [6] reported that the non-edible vegetable oils like *Jatropha, Pongamia*, *linseed, mahua* and *rice bran* oil are potential feed stocks for biodiesel production. But the main obstacle in using SVOs as fuel is its poor oxidation stability and its poor performance under cold climatic condition due to their high viscosity. Due to poor oxidation stability these oils do not remain stable after certain period of time. Further under cold climatic condition the oil particles are solidified and lead to the plugging of fuel filters lines and create fuel starvation problem for the engine. There is therefore need to assess the potentially of SVOs for direct use as well for biodiesel production on the basis of OSI the SVOs with higher OSI, not the one having low OSI can be recommended for biodiesel as the later would require exhaustive and costly attempts for stabilization. The literature reveals that no work is reported on potential assessment of vegetable oils for biodiesel production based on oxidation stability in India. This review work would enable one to select only those oils that have high OSI and recommend them for biodiesel production because the resulting biodiesel would have the stability similar to its parent oil. The work reported would not recommend oils having lower OSI for biodiesel production because the resulting biodiesel will need considerable effort for its stabilization by the addition of costly antioxidants and metals as additives but recommend potential SVOs for biodiesel production based on OSI.

2. Straight vegetable oil (SVO)

The possibilities of using edible oil resources for biodiesel production are remote as the primary need is to meet the food demand of edible oils which are already been imported in India. Further India produces about 9.3% edible oil of world's total oil seed production and fourth largest edible oil producing country in the world and still about 46% of it is imported to meet the domestic needs. Attention has, therefore, been focused to grow oil resources like *Jatropha curcas, Pongamia pinnata, neem, sal, mahua* which may be available for use as SVO for biodiesel production. Vegetable oils are mainly composed of triglycerides consisting of one mole of glycerol linked to three mole of fatty acids having long chain of carbon atoms, with single and double bonds with a carboxyl group. Despite different chemical compositions, SVOs have fuel properties similar to petroleum-diesel making them suitable as fuel for diesel engine. SVOs have several advantages over petroleum fuel viz: (i) local availability, (ii) renewability, (iii) relatively high heating value, (iv) lower sulphur content, with minimum pollution, (v) lower aromatic content and (vi) high biodegradability [7]. Atabani et al. [8] found that there is a huge chance to produce biodiesel from non-edib le oil sources. Li et al. [9] observed the use of SVO reduce particulate emission from diesel engine. Esteban et al. [10] reported that the viscosity of SVO is a major problem in its use as engine fuel. Esteban et al. [11] reported the disadvantages of SVOs like higher kinematic viscosity and surface tension, thereby making their injection and atomization difficult in engine cylinder.

2.1. Vegetable oils as food

Fats and oil are essential component of human and animal diet and provide concentrated source of energy, soluble vitamins and make the food more palatable. The principle source of fats includes vegetable fats and oils, meat, dairy product, fish and nuts. Fatty acids are the building blocks of lipid. Saturated fatty acids, available primarily in product derived from animal sources are used to raise the levels of low density lipoprotein cholesterol in the blood. The unsaturated fatty acid is characterized by the presence of one, two or more double bonds in the carbon chain and are found mostly in plant and sea food. The common vegetable oil like *soybean, sunflower, safflower, mustard, olive, rice bran* being less saturated is considered as "good fats." These acids are not highly soluble in water, and can be used as energy inside the cells. The main problem of polyunsaturated oil is that they contain extremely fragile and unstable long chain fatty acid. The unsaturated oil in semi-cooked food becomes rancid in just a few hours even when refrigerated. These are responsible for the toxicity of leftover food. As soon as such polysaturated vegetable oils enter into the body, it is exposed to temperature high enough

Table 1
Fuel properties of SVOs [14–20].

Type of oil	Vegetable oils	Specific gravity at 150	Kinematic viscosity (cSt) (38 °C)	Flash point (°C)	Cetane number	Heating values (MJ/kg)	Cloud point (°C)	Pour point (°C)
Edible oils	*Castor*	0.970	29.7	229	51.2	39.5	−11.6	−31.7
	Canola	0.916	20.6	232	40	25	−3.9	−31.6
	Cottonseed	0.914	33.5	234	41.8	39.5	1.7	−15.0
	rapeseed	0.911	37.0	246	37.6	39.7	−3.9	−31.7
	Soybean	0.913	32.6	254	37.9	39.6	−3.9	−12.2
Non-edible oils	*Mahua*	0.880	30.4	226	52.4	41.82	13	15
	Neem	0.961	22.6	175	32	40	22	11
	Jatropha	0.912	55 (30 °C)	240	40–45	39–40	16	–
	Pongamia	0.882	55 (30 °C)	110	51	46	23	–
Petroleum diesel	*Diesel*	0.82–0.86	1.3–4.1	60–80	40–55	42	−15 to −5	−33 to −15

Table 2
Composition of fatty acids in different SVOs [15–20].

S.No	Mol. formulae	*X:Y*	Saturated/ unsaturated	Edible oils					Non-edible oils			
				Canola	*Castor (Ricinus communis)*	*Cottonseed (Gossypium)*	*Rapeseed (Brassica napus)*	*Soybean (Glycine max)*	*Jatropha (Jatropha curcas)*	*Karanja (Pongamia pinnata)*	*Mahua (Madhuca indica)*	*Neem (Azadirachta indica)*
1	$C_8H_{16}O_2$	**8:0**	Saturated	–	–	–	–	–	–	–	–	–
2	$C_{10}H_{20}O_2$	**10:0**	Saturated	–	–	–	–	–	–	–	–	–
3	$C_{12}H_{24}O_2$	**12:0**	Saturated	–	–	–	–	0.08	–	-	–	0.40
4	$C_{14}H_{28}O_2$	**14:0**	Saturated	–	–	0.72	0.04	0.12	0.15	–	0.15	0.18
5	$C_{16}H_{32}O_2$	**16:0**	Saturated	4.51	1.38	25.93	4.07	11.44	14.42	10.89	22.23	17.57
6	$C_{17}H_{34}O_2$	**17:0**	Saturated	0.14	–	–	0.07	–	0.08	–	–	–
7	$C_{18}H_{36}O_2$	**18:0**	Saturated	2.00	1.11	1.74	1.55	4.14	5.82	7.89	22.49	16.60
8	$C_{20}H_{40}O_2$	**20:0**	Saturated	0.62	0.25	0.22	0.87	0.33	0.09	1.82	1.01	1.18
9	$C_{22}H_{44}O_2$	**22:0**	Saturated	0.35	–	0.11	0.27	0.27	0.14	4.11	–	0.15
10	$C_{24}H_{48}O_2$	**24:0**	Saturated	0.16	–	–	–	0.13	1.47	1.33	–	–
11	$C_{16}H_{30}O_2$	**16:1**	Monounsaturated	0.36	–	0.36	0.23	0.16	0.69	–	–	–
12	$C_{18}H_{34}O_2$	**18:1**	Monounsaturated	60.33	3.35	15.98	62.24	23.47	42.81	53.56	39.01	45.83
13	**OH** $C_{18}H_{34}O_3$	**18:1**	Monounsaturated	–	88.07	–	–	–	–	–	–	–
14	$C_{20}H_{38}O_2$	**20:1**	Monounsaturated	1.49	0.42	0.07	1.09	0.22	0.10	1.15	–	–
15	$C_{22}H_{42}O_2$	**22:1**	Monounsaturated	0.42	–	–	0.71	0.07	–	–	–	–
16	$C_{18}H_{32}O_2$	**18:2**	Diunsaturated	21.24	4.84	55.12	20.61	53.46	35.38	21.34	14.87	17.79
17	$C_{18}H_{30}O_2$	**18:3**	Polyunsaturated	9.49	0.56	0.16	8.72	6.64	0.23	2.09	0.10	0.72
% Saturated fatty acids				7.78	2.74	28.72	6.87	16.51	22.17	26.04	45.88	36.08
% Unsaturated fatty acids				92.22	97.26	71.28	93.13	83.49	77.83	73.96	54.12	63.92

to cause its decomposition when combined. To improve the oxidation stability there is need to increase the melting point and reduce its rancidity, vegetable oils with high unsaturation are usually hydrogenated so that the saturated oil/fats can be used as food with minimum chance of its quality degradation. Saturated fatty acid keeps the skin healthy, prevent early ageing, promote weight loss and assist adrenal gland to help regulate the body weight [12].

2.2. Fatty acid in SVOs

The fatty acid composition of five edible oils and four non-edible oils as given in Table 2 indicates that linoleic acid is largely available in *Soyabean* (28.1–54.3%), *Sunflower* (27.2–38.8%) and *Safflower* (30.5%) while the oleic acid is predominant in *Ground nut* (40.6%) and in *Olive oil* (65.56%).The presence of oleic acid in diet is very useful as it is effective in lowering the cholesterol content. Erucic acid is predominantly found in *Mustard oil* (24.3–37.2%) while the Lauric acid is a major component of *Coconut oil* (44.6%). Oleic and linoleic acids are predominantly present in sesame oil and *Rice bran oil*. *Sesame oil* contains (34.4–45.5%) of oleic acid and (36.9–47.9%) of linoleic oil. *Palm oil* contains Palmitic and Oleic acid in the range of (33.2–35.8%) and (31.9–35.5%) respectively. α-Linolenic acid found in the *Soyabean oil* (6.3–14.2%) and *Mustard oil* (2.9–10.5%) improves omega 6/omega 3 fatty acid ratio in the diet. Omega 3 fatty acid helps to reduce the risk of fatal ischaemic heart attack through its antiarrythmic effect [12].

2.3. Fuel properties of SVO

Out of various SVOs, the edible oil like *Castor, Canola, Cottonseed, rapeseed, Soybean* and non-edible oil like *Jatropha, Pongamia, Mahua, Neem* were selected to determine their suitability as engine fuel and for biodiesel production. There are many other SVOs available but these oils were taken because of their abundant availability in Indian subcontinent. The SVOs have the potential to be used as engine fuel but have number of disadvantages. High oil viscosity is one of the serious problems and leads to carbon deposit on injectors and valve seat, poor fuel atomization, and incomplete combustion. Consequently, carbon deposition on piston rings and cylinder wall results in the dilution and thickening of the lubricating oil that may break or cause the failure of some mechanical parts of the engine. The problem of high viscosity can be minimized by preheating the vegetable oils, blending of vegetable oils with diesel fuel, and dual-fuelling [13]. The fuel properties of edible and non-edible SVOs are given in Table 1 which shows that the kinematic viscosity of oils varies in the range from 22 at (38 °C) to 55 at (30 °C) due to high molecular weight (600–900), which is three times higher than the diesel. The flash point is very high (above 200 °C) while the higher heating values are in the range of 39–40 MJ/kg. The table also indicates that *canola oil* (edible oil) has the lowest viscosity of 20.6 cSt at 31 °C, but higher than the diesel indicating that it can be used as engine fuel. Further the cloud point is −11.6 °C for *castor oil* indicating that it will not pose any serious problem during engine operation under cold climate and so can be used as engine fuel.

As indicated above the higher viscosity is one of the main reason that the use of SVOs directly as engine fuel creates problem like piston ring sticking, gum formation and fuel atomization. These problems can be eliminated/reduced by modifying the SVO by its conversion to low viscosity biodiesel through transesterification. The composition of fatty acids of SVOs based on the literature is given in Table 2.

Table 2 shows that *cotton seed*, *Jatropha*, *Pongamia*, *mahua* and *neem* has saturated fatty acids contents ranging from 22% to 46% indicating that the relative stability is higher than SVOs having higher unsaturation i.e. *castor* and *soyabean*. These SVOs are expected to easily degrade with time i.e. less stable from chemical transformation point of view. Similar trend may be expected by the biodiesels produced from these oils. Further it is also seen that *castor oil* contains more than 88% of monosaturated oleic acid which is not present in any of the oil and has therefore less viscosity than other oils with polyunsaturated fatty acids. As the percentage of saturated fatty acids in oil increases the oxidation stability tends to increase while the cold flow properties become poorer [21]. So the oils having low saturated and high unsaturated fatty acid cannot be recommended as fuel like *Jatropha, Pongamia* in case of non-edible oils while *castor oil* (edible oil) can be recommended as fuel due to higher saturation. Therefore, SVOs having high % saturation like *Mahua* and *Neem* can be

recommended for biodiesel production due to higher stability and market acceptability as the resulting biodiesel would not need to be stabilized using antioxidants/other catalysts while the other oils are not recommended for biodiesel production and are not potential feed stocks. The % saturation and unsaturation can be used to access the oxidation stability of oils as discussed below.

3. Oxidation stability (OS)

The oxidation stability of fats, oils and their products plays an important role in determining the quality and so is an important parameter for quality assessment of fats and oils and biodiesels derived from them. It is defined as the resistance of oil/fats/biodiesel to degrade by oxidation with air. The OS is distinguished from storage stability is that oxidation may occur not only during storage but also during production and usages. The oil and fats with high unsaturation are more susceptible to radical attack as a first step of oxidation. Therefore an understanding of fuel stability requires the knowledge of chemical composition of biodiesel and its parent's oil/fat. The oxidation of fatty acid is related to the degree of double bond which can be correlated to the reduced oxidation stability of the fuel and so, the fuel instability is directly proportional to the number of double bonds. Generally, the polyunsaturated fatty acids (C18:2, linoleic acid; C18:3 linolenic acid) are most susceptible to oxidation than fatty acid having one or two double bond [22]. The fuel stability depends on (i) oxidation or auto-oxidation due to its exposure to its ambient air, (ii) thermal or thermal-oxidative decomposition from excess heat, (iii) hydrolysis from contact with water or moisture in tanks and fuel lines or (iv) microbial contamination from the migration of dust particles or water droplets containing bacteria or fungi into the fuel [23].

Arain et al. [24] stated that the stability of oil/fuel quality for longer time is an important requisite to control the quality of oil fats and biodiesel in industries. Shelf life of vegetable oils influences their suitability and market value. The consequence of lipid oxidation leads to the reduction in fuels shelf life and is one of the serious issues in food industry. Jain and Sharma [25] reported that there are various types of stabilities like oxidation, storage and thermal, playing key roles in making the fuel unstable. All fats and oils are prone to oxidation. The rapidity of oxidation depends on the degree of unsaturation, the presence of antioxidants, and prior storage conditions [26]. This auto-oxidation caused by contact with air during long term storage presents a legitimate concern for monitoring of oil/fuel maturity and its effect on kinematic viscosity, acid value or peroxide value. The exposure of oil fats or biodiesel to atmosphere O_2, heat, heavy metal, light, porphyrims, etc. generate free radicals that form peroxide radicals which subsequently led to the formation of stable secondary products. The oxidation stability can be measured by Oil Stability Index or Oxidation Stability Index (OSI) as discussed below.

3.1. Measurement of OSI

The OSI method is based on determining the time usually, called induction period (IP) and is widely used in fats and oil industries and can be measured by American Oil Chemists Society (AOCS) method using Rancimat and Differential Scanning Calorimetric (DSC) measurement by passing stream of air through the oil or fuel sample contained in a sealed and heated reaction vessel. The air oxidation of oil/fats results in the formation of peroxides as the primary oxidation products. Secondary oxidation products formed after the complete destruction of the fatty acids including low-molecular organic volatile acids are carried with the stream of air to a second vessel containing deionised water whose conductivity is continuously recorded. The presence of volatile acids is detected by the increase in conductivity. The time that elapses until these secondary reaction products appear is known as the induction time, induction period or Oil Stability Index (OSI) [27]. Jain and Sharma [25] and Shabuddin et al. [28] have reported that the difference in oxidation stability of different oils is due to the difference in the amount of saturated fatty acids present in the molecule. The presence of water may hydrolyse the oil molecule [22]. The authors have developed a method for the measurement of OS of oil/Biodiesel and the details are available in [20].

3.2. Mechanism of oxidation

The oxidation stability of oil/biodiesel is affected by degree of unsaturation imparting high level of reactivity with O_2 when it comes in contact with air /water [29]. The methylene groups adjacent to double bonds are, particularly, more susceptible to free radical attack as the first step in the fuel oxidation [30]. The rate of oxidation of fatty compounds depends on the number of double bonds and their position [31]. The mechanism of oxidation is already described in the paper [20].

3.3. APE and BAPE

OSI is a function of two type of position equivalent w.r.t. to double bond APE and BAPE

An Allylic Position equivalent (APE) group consist of methylene ($-CH_2-$) attached to a vinyl group ($-CH{=}CH_2$). An Allylic carbon is a carbon atom bonded to a carbon atom that, in turn, is doubly bonded to another carbon atom. Bis Allylic Position Equivalent (BAPE) is given by hydrogen atom bonded to same carbon atom that are in allylic position w.r.t. to two different C=C double bonds i.e. $=CH{-}CH_2{-}CH=$

The chemical structure of oleic acid, linoleic acid and linolenic acid giving APE and BAPE is shown in Table 3.

The fatty acids with allylic centres are more prone to auto-oxidation, as the free radicals formed during oxidation are stabilized by resonance. Oleic acid contain two APE, linoleic acid contain two APE and one BAPE while linolenic acid contain two APE and two BAPE. So the linolenic acid is more susceptible to oxidation followed by linoleic and oleic acid. So the order of oxidation rate is given by

Linolenic acid > Linoleic acid > Oleic acid

Further the numbers of BAPE are more prone to oxidation and hence the oil with more BAPE is more prone to oxidation than the oil having APE [32–34].

Table 3
Number of APE and BAPE in typical free fatty acid.

Common name	Molecular Formula	Molecular structure	APE	BAPE
Oleic acid	$C_{18}H_{34}O_2$	$CH_3\,(CH_2)_6\,CH_2\,CH{=}CH\,CH_2\,(CH_2)_6\,COOH$	2	0
Linoleic acid	$C_{18}H_{32}O_2$	$CH_3(CH_2)_3\,CH_2CH{=}CH\,CH_2CH{=}CH\,CH_2\,(CH_2)_6\,COOH$	2	1
Linolenic acid	$C_{18}H_{30}O_2$	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2(CH_2)_6COOH$	2	2

Legend: light colour, APE; dark colour, BAPE.

Table 4
Computation of APE, BAPE and OSI of SVOs based on % unsaturation.

Type of oil	% Unsaturation				Stability parameter		
	Name of SVO	% $C_{18:1}$	% $C_{18:2}$	% $C_{18:3}$	APE	BAPE	OSI (h) at 110 °C
Edible oils	*Canola*	60.33	21.24	9.49	188.12	40.22	2.1
	Castor	3.35	4.84	0.56	17.5	5.96	3.6
	Cottonseed	15.98	55.12	0.16	142.52	55.44	1.4
	Rapeseed	62.24	20.61	8.72	183.14	38.05	2.1
	Soya bean	23.47	53.46	6.64	167.14	66.74	0.9
Non-edible oils	*Jatropha*	42.81	35.38	0.23	156.84	35.84	2.2
	Karanja	53.56	21.34	2.09	153.98	25.52	2.7
	Mahua	39.01	14.87	0.10	107.86	15.07	3.2
	Neem	45.83	17.79	0.72	128.68	19.23	3.0

Table 5
% Saturation and Unsaturation, CP, CFPP and OSI of different SVOs.

Category of oil	Name of oil	% Saturated fatty acid	% Unsaturated Fatty acid	OSI (h) at 110 °C	CP (°C)	CFPP (°C)
Edible oils	*Castor*	2.74	97.26	3.6	−20.8	−22.5
	Rapeseed	6.87	93.13	2.1	−14.9	−17.4
	Canola	7.78	92.22	2.1	−13.5	−16.2
	Cotton seed	28.72	71.28	1.4	16.5	9.4
	Soyabean	16.51	83.49	0.9	−1.02	−5.5
Non-edible oils	*Jatropha*	22.17	77.83	2.2	7.1	1.3
	Karanja	26.04	73.96	2.7	12.6	6.1
	Neem	36.08	63.92	3	27.1	18.4
	Mahua	45.88	54.12	3.2	41.2	30.5

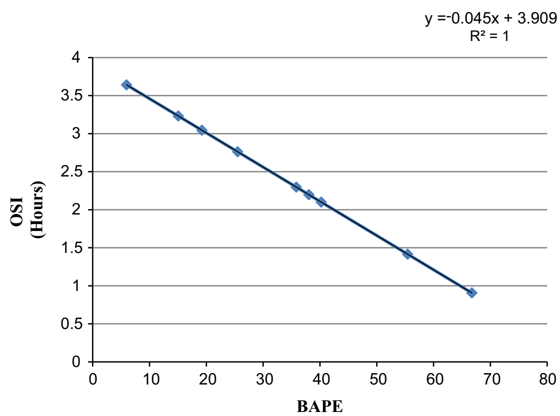


Fig. 1. Variation in OSI with BAPE.

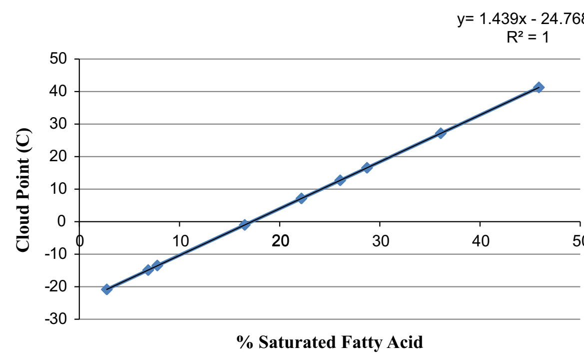


Fig. 2. Variation of cloud point and % saturated fatty acid.

3.4. *Calculation of APE, BAPE and oxidation stability of SVO*

Chemically the stability of SVO can be theoretically measured using APE and BAPE in triglyceride molecule. The rate of oxidation of fatty compounds depends on the number of double bonds and their positions. The oxidation chain reaction is usually imitated at the positions allylic or bis allylic to double bonds. APE is a theoretical measure of the number of singly allylic carbons present in fatty oil or ester, assuming that all poly-olefinic unsaturation is methylene-interrupted BAPE is also a similar theoretical measure of the number of doubly allylic carbons present in the fatty oil or ester structure. Both APE and BAPE can also be calculated and correlated with Oxidation Stability Index (OSI) using the following equation [20]:

$$APE = 2 \times (\%\ C18{:}1 + \%\ C\ 18{:}2 + \%\ C\ 18{:}3) \quad (1)$$

$$BAPE = \%\ C\ 18{:}2 + (2 \times \%\ C\ 18{:}3) \quad (2)$$

$$OSI = 3.91 - (0.045 \times BAPE) \quad (3)$$

The APE and BAPE and OSI of SVO based on the data of Table 2 has been calculated and is given in Table 4 [20].

These data indicate that OSI of SVOs in order of decreasing OSI are *Castor* > *Mahua* > *Neem* > *Karanja* showing that these oil may be considered as potential feed stocks for biodiesel production in terms of OSI and the resulting biodiesel would be stable accordingly while others are relatively more unstable. The variation of OSI with BAPE as shown in Fig. 1 gives coefficient of variation (R^2) of 1 showing that significant correlation exist between BAPE and OSI and therefore BAPE can be used to predict the OSI of any oil/biodiesel and can be used to grade different SVOs from point of oxidation stability. This is agreement with the work of Dunn [31] who showed that BAPE significantly affect the OSI of oil as well as biodiesel. More the number of BAPE in the oil, more it is prone to oxidation. From Table 4 it is clear that *Castor* oil (edible) has highest OSI (3.6 at 110 °C) followed by *Mahua* (3.2), *Neem* (3.0) and *Karanja* (2.7 h) while the other SVOs have lower OSI.

The above finding reveals that the SVOs in order of decreasing OSI i.e. *Castor* > *Mahua* > *Neem* > *Karanja* can be recommended as potential feedstock for biodiesel production from the point of Oxidation stability while other SVOs are not due to their instability as the resulting biodiesel would require considerable effort to enhance the fuel stability.

4. Cold flow properties of SVOs

The SVOs under cold climatic condition may lead to its condensation and gel formation resulting in the crystallization of fuel particles in liquid fuel due to strong intermolecular interaction below their melting point. Crystallization occurs in two interrelated steps nucleation and crystal growth. The former is the first stage of crystallization and occurs when the fuel molecules come together to initiate the formation of crystal lattices, which further grow by the nucleation of the layers of new lattices on the existing ones to form larger crystals. The process continues until a continuous network of crystals is formed and the fuel flow to the engine is reduced and the engine start experiencing fuel starvation and incomplete fuel combustion and finally it ceases to stop. The following are the cold flow properties of SVOs:

4.1. *Cloud point (CP)*

Cloud point (CP) is the temperature at which the turbidity starts appearing. This turbidity starts increasing the viscosity of the fuel. When such fuel is used in the engine problem of clogging of fuel filters and injectors starts. Therefore, CP indicates the

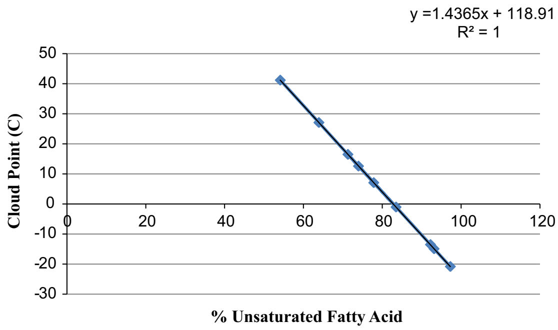


Fig. 3. Variation of cloud point and % unsaturated fatty acid.

tendency of the oil to plug the filters or small orifices at cold operating conditions. This tendency ultimately results in the stoppage of the engine. The CP can be calculated by [17]

$$CP = 1.44 \times Y - 24.8 \quad (4)$$

where Y is the amount of % saturated fatty acid present in the oil.

4.2. Pour point (PP)

It is the lowest temperature at which the fuel becomes semi-solid and loses its flow characteristics and is the measure of the fuel gelling point. The PP is always lower than the CP.

4.3. Cold filter plugging point (CFPP)

It is the lowest temperature at which a given volume of liquid fuel still passes through a standard filtration device in a specified time, when subjected to cooling under certain conditions. This measures the lowest temperature at which a fuel gives trouble free flow in a fuel system. It is very important for cold climatic countries, where high CFPP clog up the vehicle engines more easily. CFPP is calculated by following equation [17]:

$$CFPP = 0.8537 \times CP - 4.72 \quad (5)$$

where CP is obtained from Eq. (4), the CP and CFPP are calculated using the data of Table 4 and the result are given in Table 5.

The table indicates that more the unsaturation better are the CP and CFPP. The *Castor* oil has best CP (−20.8 °C) and CFPP (−22.5 °C) of all the oils and so can be used in cold climate without any problem as engine fuel. Out of all SVOs considered, *Castor* oil is found to the highest OSI and best CP and CFPP and is best resource for biodiesel production but its availability for fuel production is questionable due to its edible nature. Fig. 2 gives the variation of CP with the % saturation in fatty acid of SVOs. It shows that CP increases with increase in % saturation indicating that the SVOs its biodiesel with high % saturation would be more problematic for engine operation due to poor cold flow properties. From Fig. 2 it is also clear that R^2 of 1 indicates significant relation of CP with % saturation and can be used to access the cold flow behaviour of oil/biodiesel on the basis of % saturation. All SVOs having CP below 0 °C can be directly used as engine fuel in cold regions without much cold flow problem. As stated above, even the SVO with good cold flow properties can be mixed with SVO having lower cold flow properties and the binary mixture can be used as engine fuels in cold climate. All SVOs having CP below 5 °C or so can be used without any problem in temperate regions and the same may be true for mixture of biodiesels.

It is also found that the chain length of fatty acids also have significant influence on the cold flow properties of SVOs as evidenced by the fact that longer the carbon chain, the higher the melting point, and poorer the low temperature performance [35–37].

The relation of CP with % unsaturated shown in Fig. 3 shows that increase in % unsaturation in oils leads to decrease in CP. The $R^2 = 1$ is indicative of the fact that the relation is valid and predictions may be made to compute CP of SVOs based on % unsaturation. Based on the above SVOs having CP and CFPP in decreasing order are found as *Castor* > *Rape seed* > *canola* > *Soyabean* in edible while in non-edible oils it is as *Mahua* > *Neem* > *Karanja* > *Jatropha* > *Soybean.* The result shows that *Mahua oil* and its biodiesel will solidify readily while *Soybean* would undergo solidification slowly and hence there is need to improve the cold flow properties by mixing the oil like *Canola* having good CFPP with the oil having bad CFPP like *Mahua* to get binary mixture of SVO with improved CFPP. The *Jatropha* and *Karanja* oil the main source of biodiesel for India needs considerable improvement in CFPP before its utilisation as engine fuel in cold regions.

5. Limitation of SVO as a direct engine fuel

Running a diesel engine on SVOs has some disadvantages of having much more viscosity different chemical or combustion properties compared to diesel. SVO can be mixed with diesel, kerosene or other fuels and solvents to reduce the viscosity of the oil. Vehicles using SVOs can have two tank systems one for diesel and another for SVO. At the start-up and shut-down the vehicle operate on diesel or biodiesel, while the SVO can only be used when the exhaust heat the second tank containing SVOs. Shutting off a diesel engine running on SVOs can cause the residue to crystallize in the cylinder and can cause problems. During cold weather condition the SVOs can crystallize at higher temperature and cause cold starting problem due to plugging of fuel filters by crystals [38–42].

6. Findings

The paper concludes that the SVOs in order of decreasing OSI are *Castor* > *Mahua* > *Neem* > *Karanja* that recommended as potential feedstock for biodiesel production from the point of Oxidation stability while other SVOs are not potential feedstock due to their instability as the resulting biodiesel would require considerable effort to make the fuel stable. The SVOs having CP and CFPP in decreasing order are *Castor* > *Rape seed* > *canola* > *Soyabean* edible oil while in the case of non-edible oil it is found as *Mahua* > *Neem* > *Karanja* > *Jatropha* > *Soybean* indicating that *Mahua* oil and its biodiesel will solidify readily while *Soyabean* would undergo solidification slowly and hence its cold flow properties need to be improved by mixing the oil like *Canola* having good CFPP with the oil having bad CFPP like *Mahua* to get a binary mixture SVO having improved CFPP. The *Jatropha* and *Karanja* oil the main source of biodiesel for India needs considerable improvement in CFPP before its utilisation as engine fuel in cold regions. The present study reveals that *Castor* oil has highest OSI and good cold flow properties and recommended as an ideal engine fuel both as SVO and its biodiesel.

7. Conclusions

The grading of oils in terms of stability and cold flow properties helps to select the potential oil resources for biodiesel production and discard the other resources that may require considerable efforts to improve the oxidation stability as well as cold flow properties. The oil stability and cold flow properties are affected mainly by OSI and CP based on the comparison of FFA of SVOs,

APE, BAPE and OSI. The stability and cold flow properties of SVOs have been theoretically predicted. The SVOs in order of decreasing OSI i.e. *Castor* > *Mahua* > *Neem* > *Karanja* are recommended as potential feedstock for biodiesel production from the point of Oxidation stability while other SVOs are not due to their instability as the resulting biodiesel would require considerable effort to make the fuel stable. CP and CFPP of edible oil in decreasing order is found as *Castor* > *Rape seed* > *canola* > *Soyabean* while non-edible oil as *Mahua* > Neem > Karanja > Jatropha > Soybean indicating that there is need to add additives to improve the cold flow properties. Castor oil is found to have highest OSI and good cold flow properties and recommended to be used as SVO for biodiesel production for us as an engine fuel. There is still considerable scope of R&D in finding the balance between OSI and CFP of SVOs as well as their biodiesel from fuel stability point of view.

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